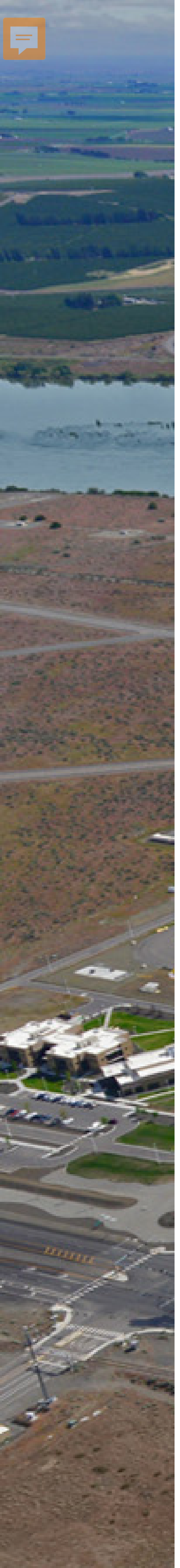

Pacific Northwest NATIONAL LABORATORY

Microscopy Investigation of the Fading Mechanism of Electrode Materials

Chongmin Wang

Vehicle Technologies Annual Merit Review

June 1-4, 2020

Project ID #bat226

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

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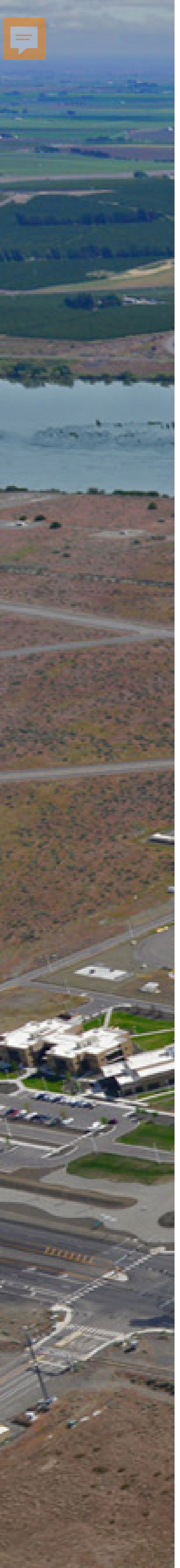


Pacific Northwest NATIONAL LABORATORY

Overview

Timeline

- Start date: Oct. 1, 2019
- End date: Sept. 30, 2022
- Percent complete: 25%

Budget

- Total project funding: $1200k
  - –DOE share: 100%
- Funding received in FY 2019: $400k
- Funding for FY20: $400k

Barriers Addressed

- Structural and chemical nature of interface in battery materials
- Interfacial controlled fading and failure mechanism of electrodes
- High theoretical capacity of electrode materials cannot be fully utilized

Partners

- Lawrence Berkeley National Laboratory
- Argonne National Laboratory
- Army Research Laboratory
- Stanford University
- National Renewable Energy Laboratory
- GM Research Center
- University of Texas at Austin
- Hydro Quebec
- Group 14 company
- Thermo Fisher Scientific Company
- Hummingbird Scientific Inc.
- Battery group in PNNL

Relevance/Objectives

- Develop *ex-situ*, *in situ*, *operando and cryo*-HRTEM, *in-situ* liquid SIMS and associated spectroscopic techniques for rechargeable battery research

- Probe the interfacial process in battery and the fading mechanism of electrode materials

- Correlate structural and chemical evolution of electrode with both interfacial process and battery performance for guided designing of new battery materials

- Obtain fundamental understanding that enables high-energy density materials required by VTO mission of long-range electrical vehicles

Milestones and Approach

- Integration of AFM cantilever into TEM column to in-situ measure Li dendrite growth force (12/31/2019, Complete)

- Establish structural and chemical feature of CEI layers in cathode and correlation with Al dopant (03/31/2020, Complete)

- Identify the correlation of SEI structure and chemistry with electrolyte composition and electrochemical operating condition (06/30/2020, On track)

- Establish the cathode stability in solid state configuration (09/30/2020, On track)

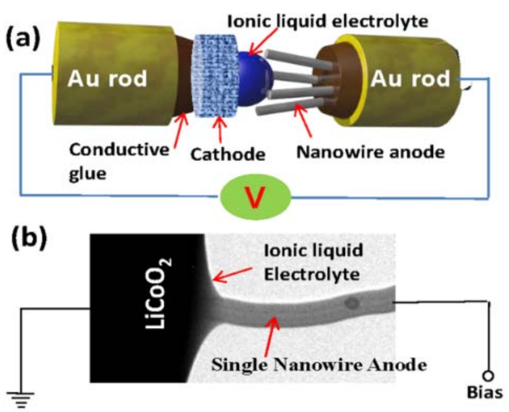
Technical Accomplishments and Progress

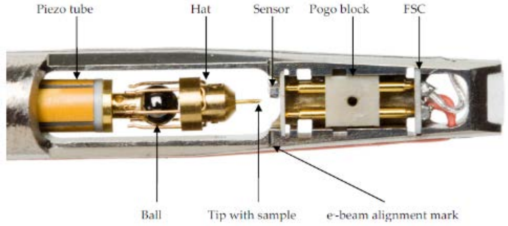
- Developed in-situ TEM capability, enabling the direct measurement of the force during the Li whisker growth
  - In-situ measured the force that a growing Li whisker will likely exert on a separator
  - In-situ observation of the nucleation and growth process of Li whiskers and their correlation with SEI layer
  - Systematically established the failure mechanism of a growing Li whisker
- Established that lithium carbonate plays a key role for development of whisker shaped Li
- Revealed the functioning role of Al in NCA
- Mapped out the spatial distribution of Al in NCA
- Answered the key question why NCA is more stable than NC even with minimal amount of Al in the system

Technical Accomplishments

Enhanced *In-Situ* environmental TEM, Cryo-TEM and *In-Situ* liquid SIMS to capture structure, atomic and molecular signature of energy materials

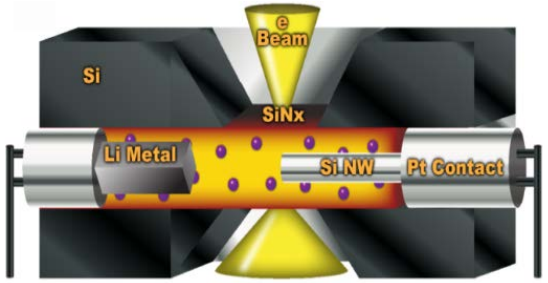
Open cell *in-situ* TEM

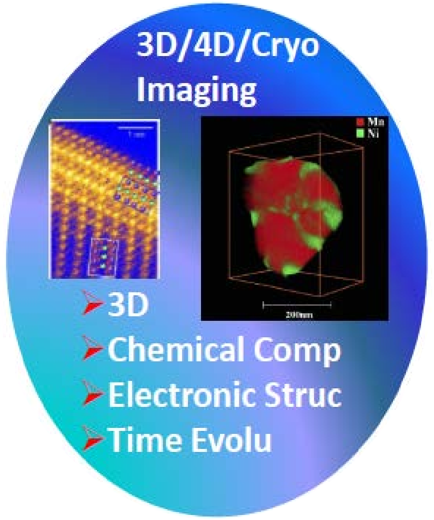




J.Y. Huang and C.M,. Wang, et al., Science, 330(2010)1515

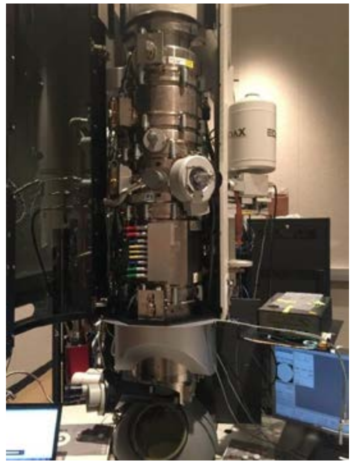
Closed cell *in-situ* TEM





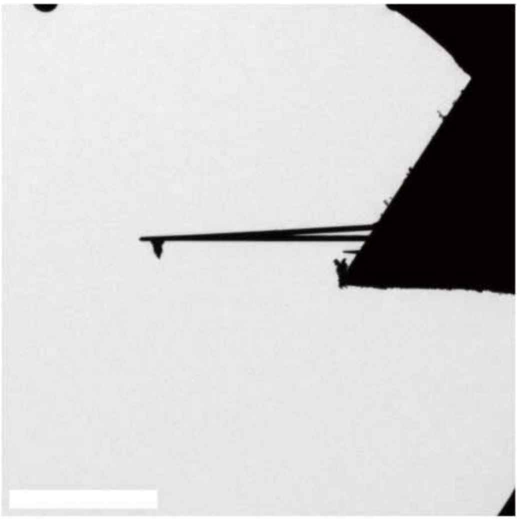
M. Gu and C.M. Wang, et al., Nano Letter, 13(2013)6106

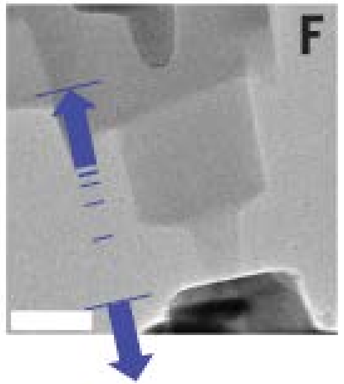
In-Situ Environmental, cryo TEM



L.L. Luo and C.M. Wang et al., Nature Nanotechnology, 12(2017)535

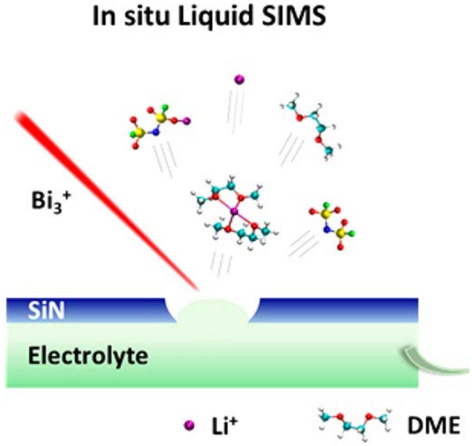
In-situ force measurement

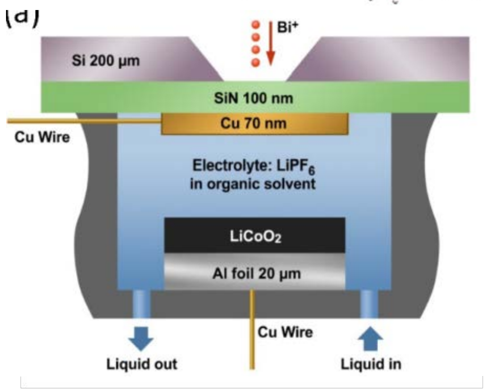


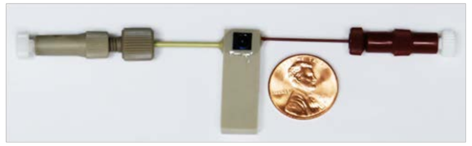


Yang et al., Nature Nanotechnology, 14, 1042-1047(2019)

In-Situ Liquid SIMS







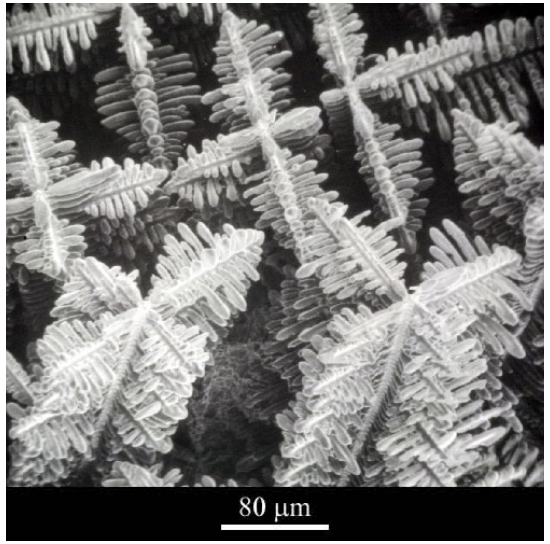
Zhou et al., Nature Nanotechnology, 2020

Towards real battery operating condition

Technical Accomplishments

Dendrites or whiskers: They really matter

Dendrite in solidified Co-Sm-Cu alloys: R. Glardon at al. J. Cryst. Growth, 51 (1981) 283-291



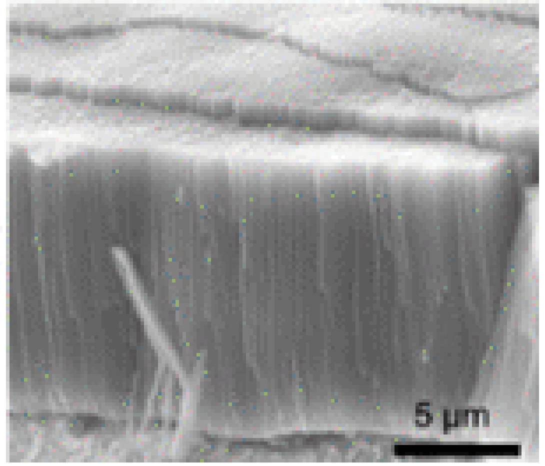
Solidification process: crystal nucleation and growth

Snowflake or Ice crystal

Crystallization: cooling rate

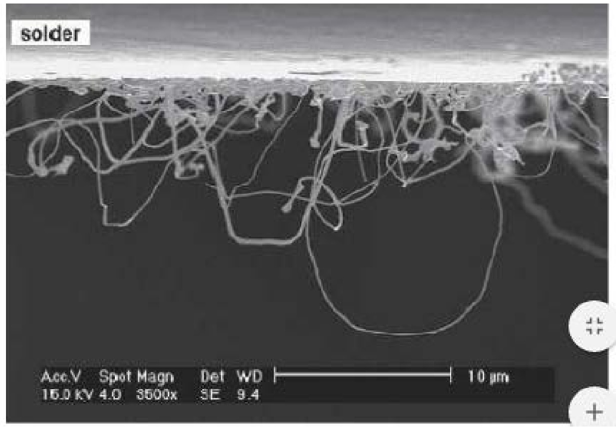
The typical morphology of Li dendrite: Chianelli et al., J. Crystal Growth,1976.

Li whisker or filament: Ren et al., ACS Energy Letters, 2017



Growth of Grass Can Pop up Asphalt Pavement

- **The root cause for Li dendrite formation?**
- **Behavior of Li whisker or filament encountered with separator**



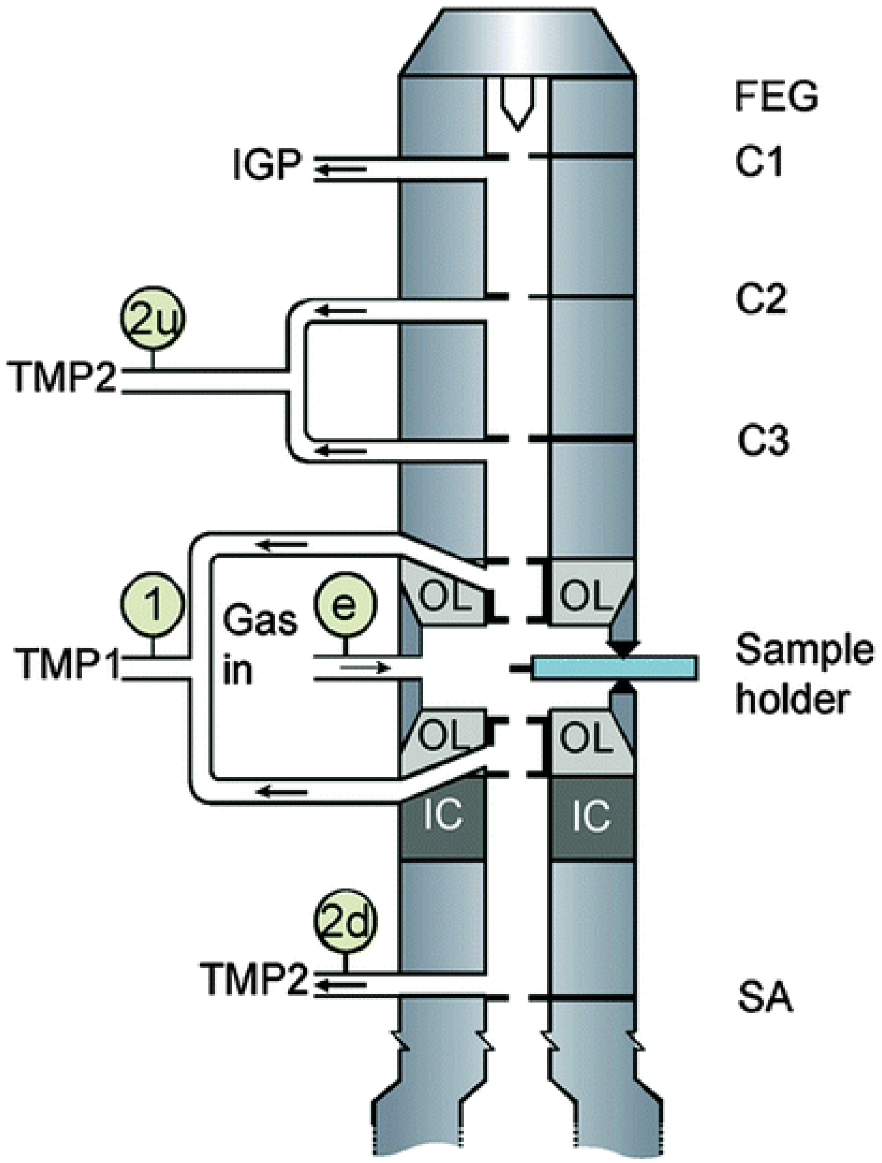
Tin whiskers in $Sn_3Ag_{0.5}Cu_{0.5}Ce$ Solder Balls; Chuang et al., J. Electro. Mater. 35, 2005.

Tin whisker formation: selective growth of Tin

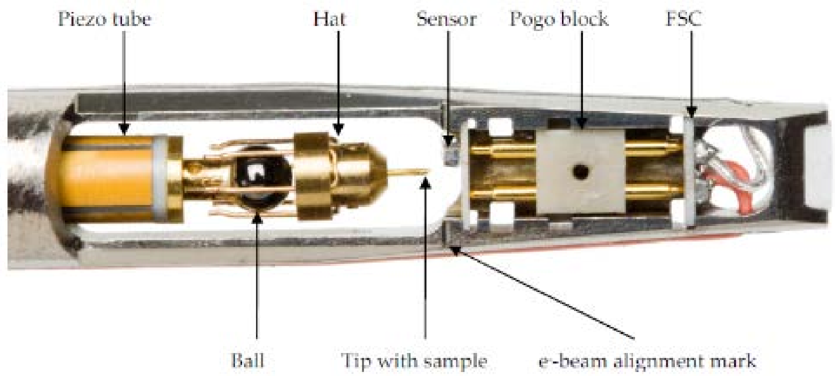
Technical Accomplishments

Integration of ETEM with force measurement

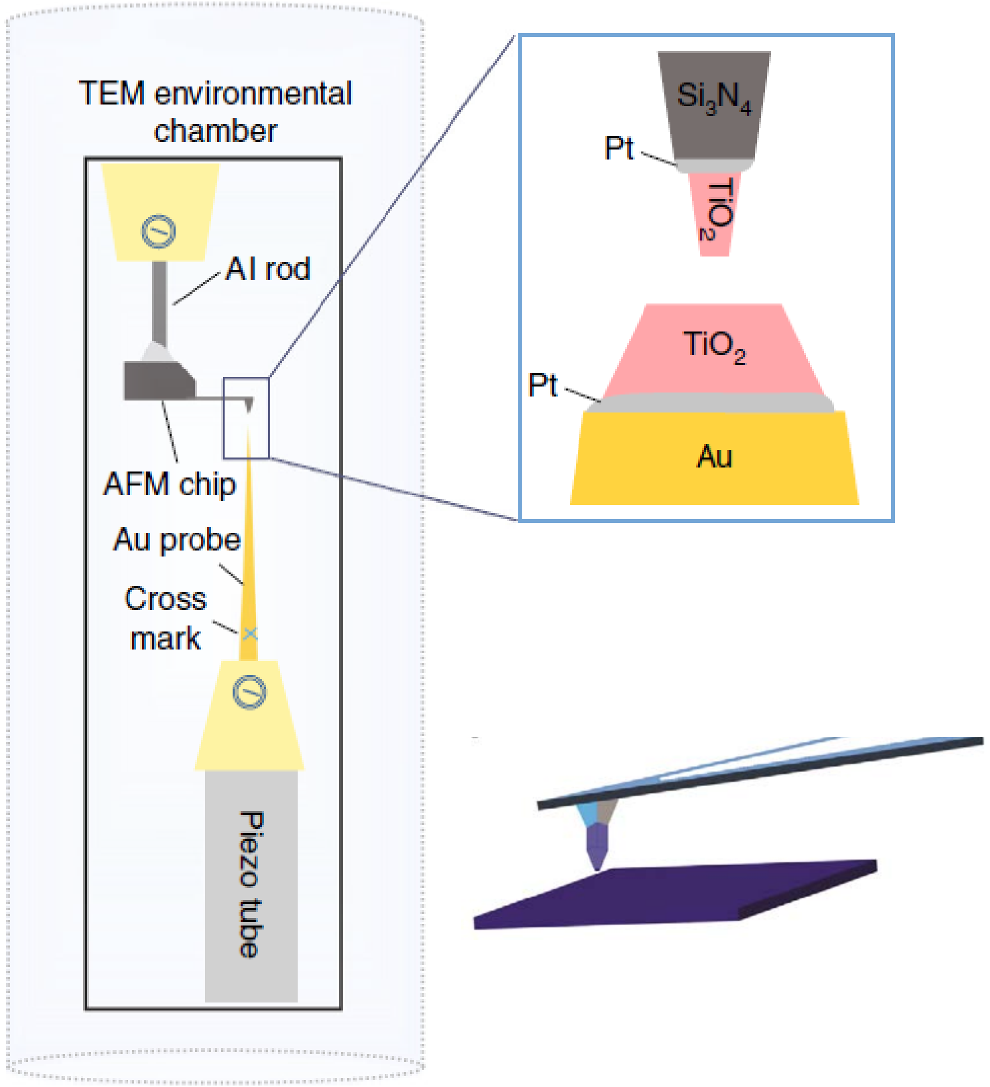
ETEM



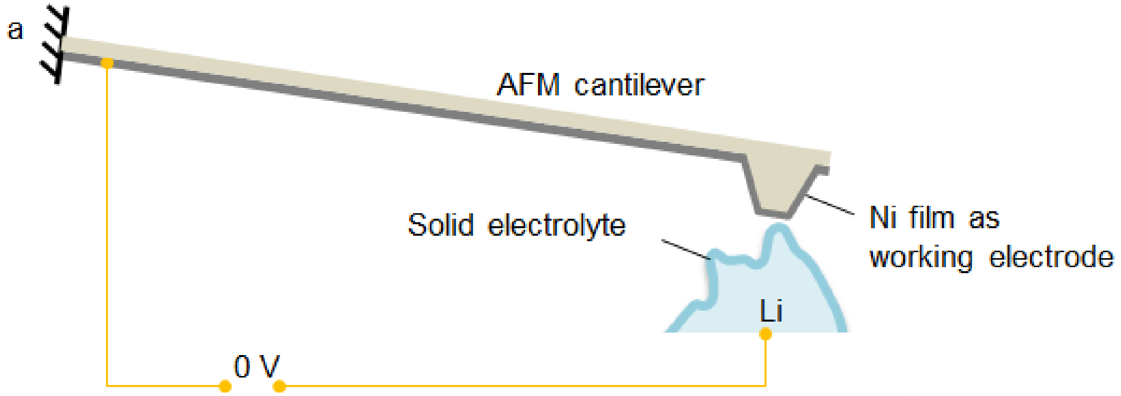
Nano-Manipulator



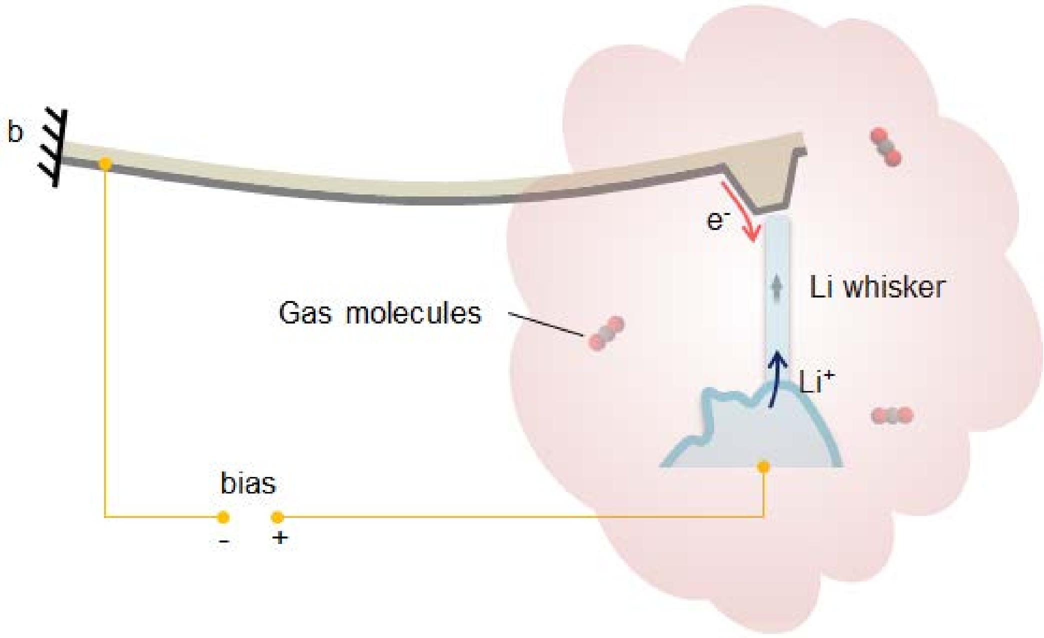
AFM Cantilever for Measuring Force



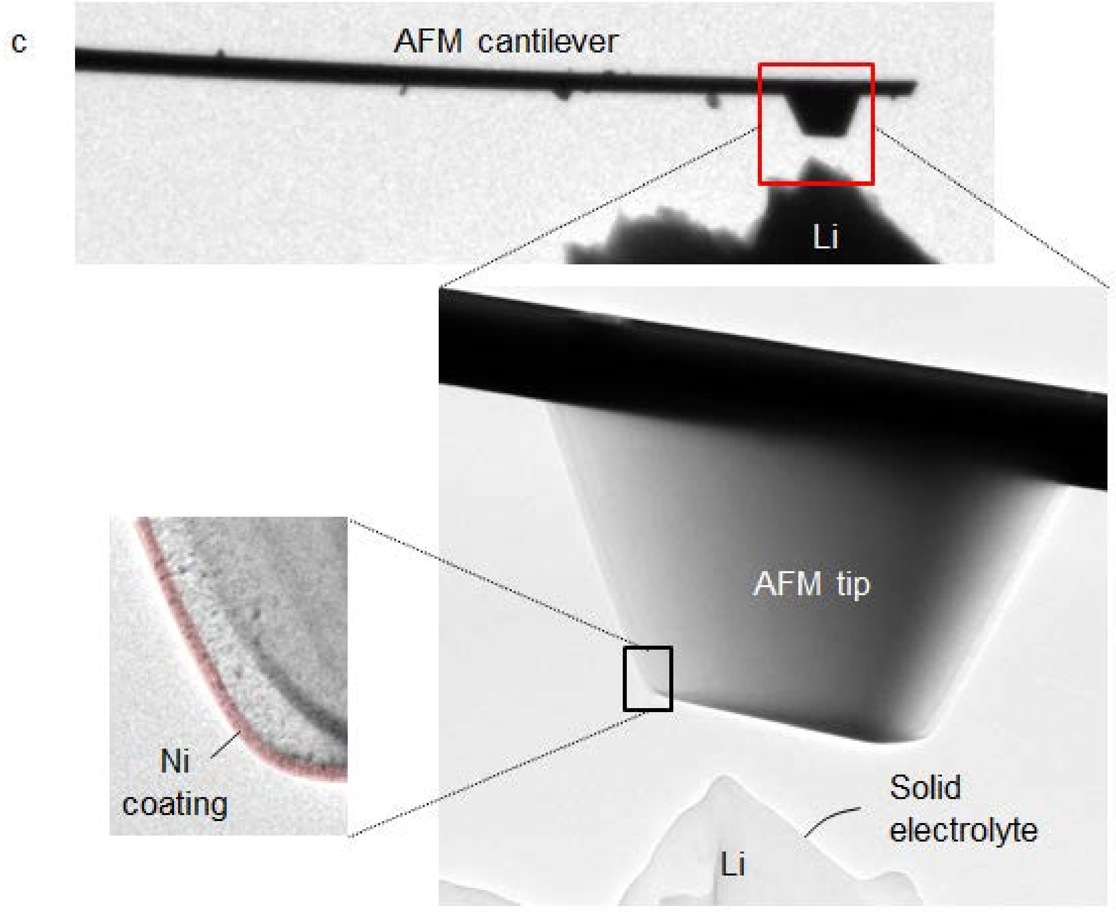
Technical Accomplishments
In-situ TEM for measuring the growth force of lithium dendrite



Experimental setup prior to the Li deposition



A growing Li whisker pushes the AFM cantilever

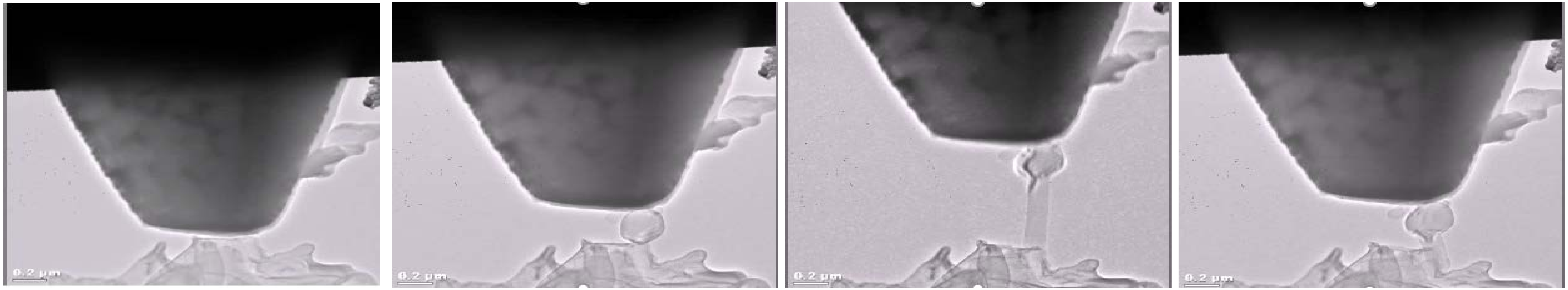


- TEM image of the in-situ battery cell in the ETEM
- The spring constant of the AFM cantilever is ~0.4 $N \cdot m^{-1}$

Yang He et al., Nature Nanotechnology, 14, 1042-1047(2019).

Technical Accomplishments

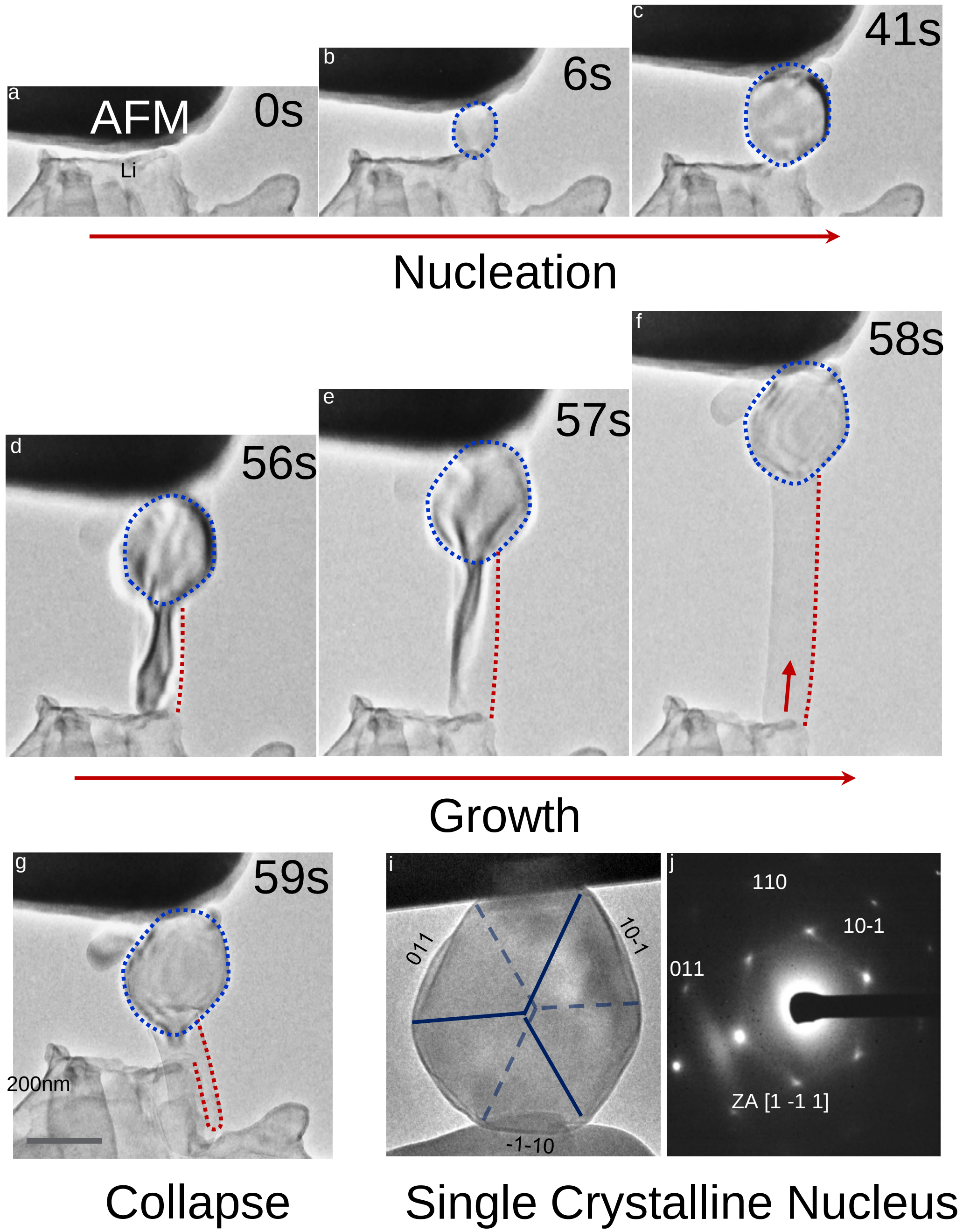
In-Situ TEM observation of Li whisker nucleation and growth in CO_2

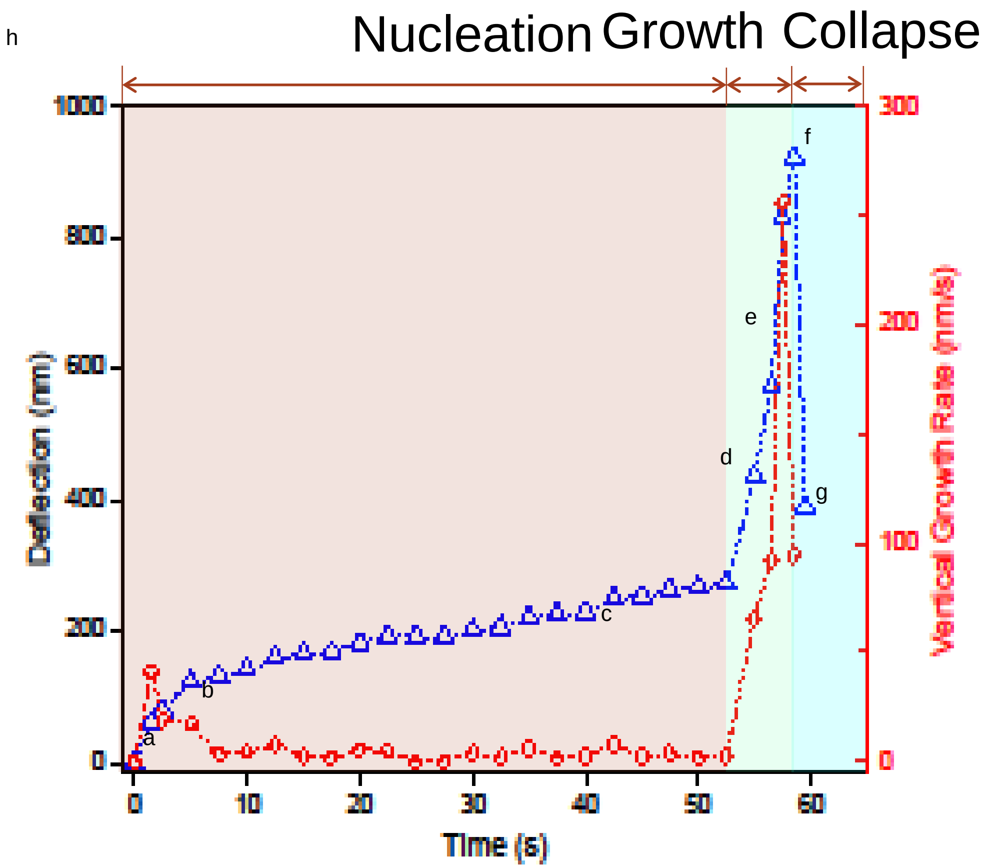


Sequential in-situ TEM images showing the nucleation of single crystalline Li nuclei formation, growth of Li whisker, and failure under stress

Technical Accomplishments

Nucleation and growth of Li dendrite in CO_2

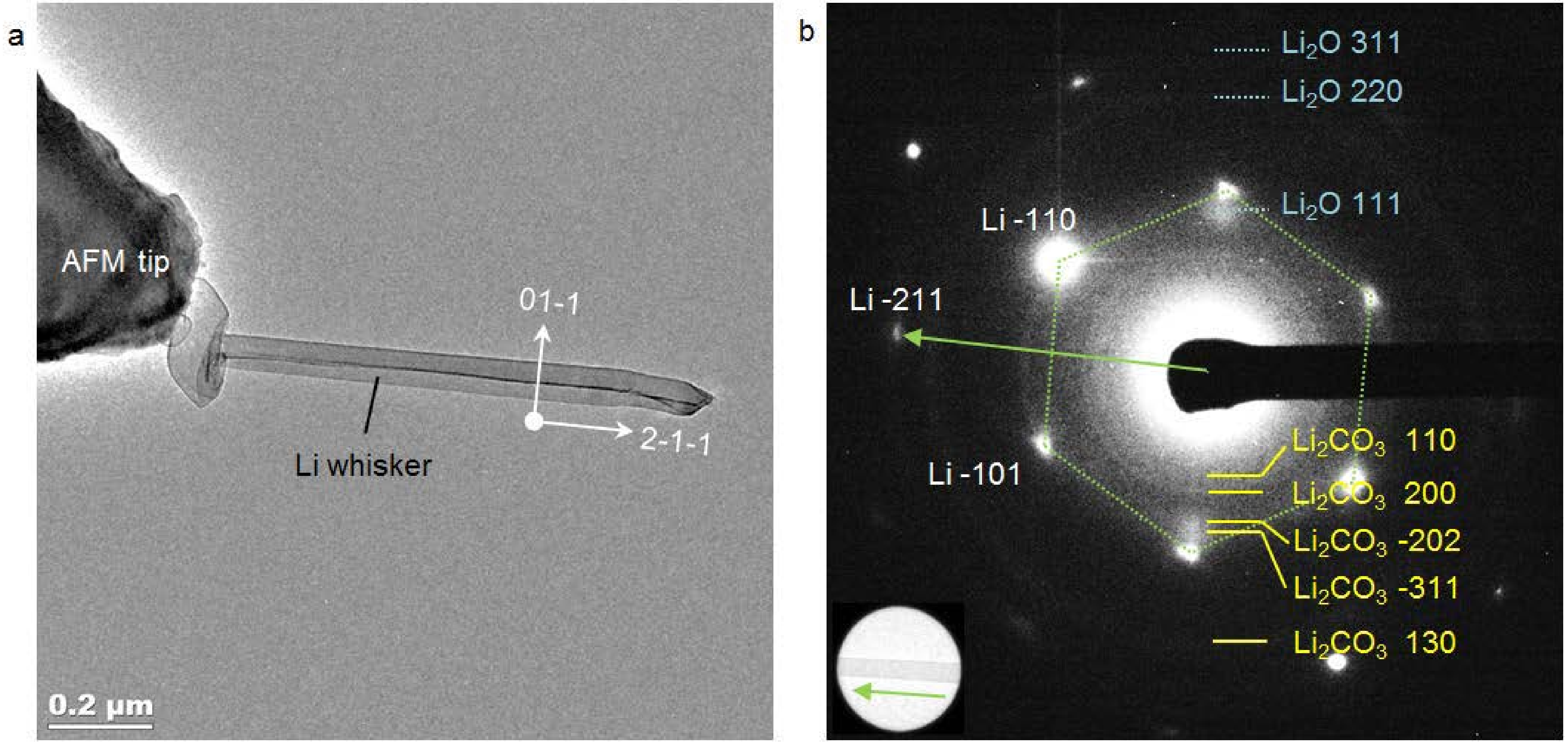




- Li whisker formation during electrochemical deposition of Li in CO_2 environment
- Sequential TEM snapshots of the Li particle nucleation
- Whisker growth process
- Whisker collapse
- Spring constant of the AFM cantilever is ~0.4 $N \cdot m^{-1}$

Technical Accomplishments

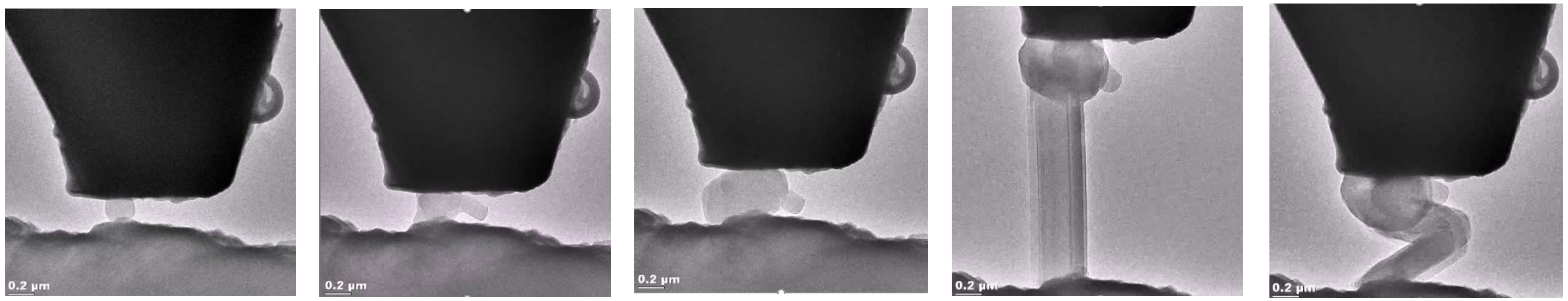
Electron diffraction analysis of the surface species and orientation of the Li whisker deposited in-situ in CO_2



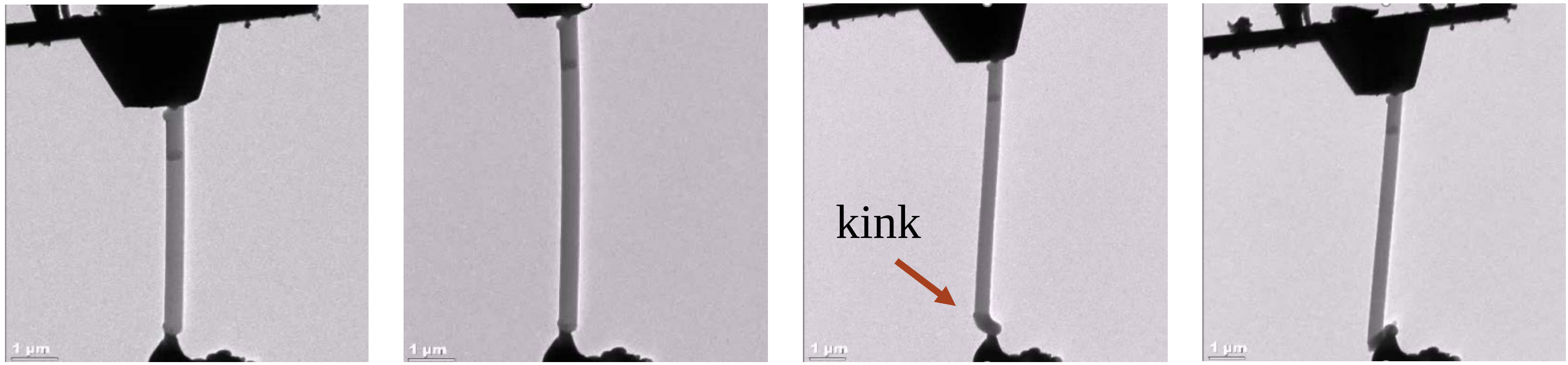
- The whisker growth direction, i.e., <-2 1 1>.
- The whisker is primarily bounded by {1 1 0} surface facets.
- The additional diffraction rings can be assigned to Li_2CO_3 and Li_2O crystals.
- The orientation relation of Li surface and Li_2CO_3 is (0 1 -1)Li // (-2 0 2)Li_2CO_3.

Technical Accomplishments

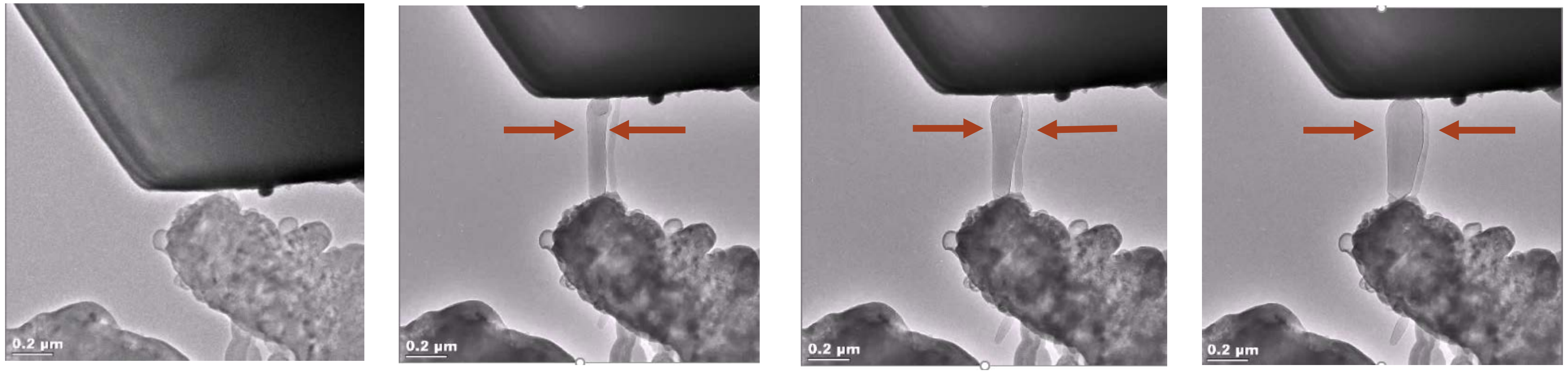
In-Situ TEM observation of Li whisker failure



- Sequential in situ TEM images showing the growth of Li whisker and eventually “failure” by buckling as the stress increases



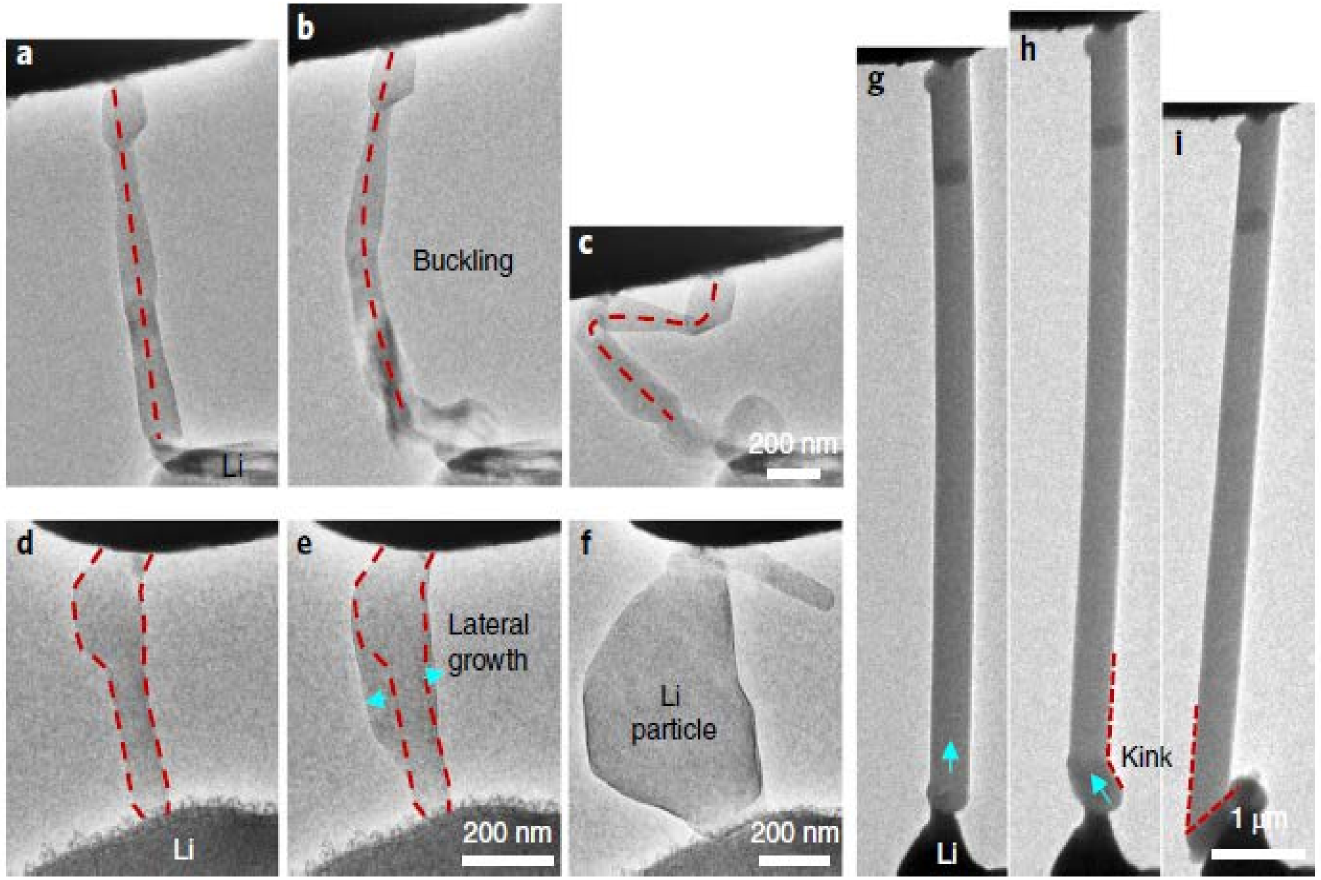
- Sequential in-situ TEM image showing the failure of a growing Li whisker through “kink” formation



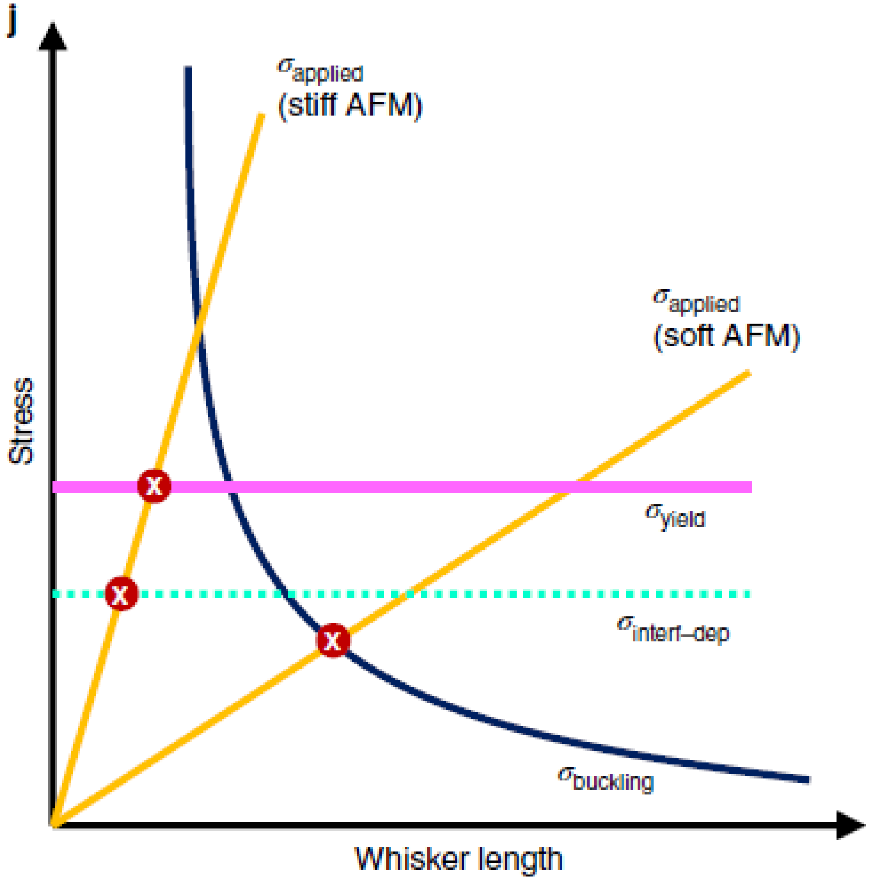
- Sequential in-situ TEM images showing the stress leads to a lateral growth as indicated by the arrows

Technical Accomplishments

Different failure mode of Li whisker



Failure Mode of Li whisker



Failure Map of Li whisker

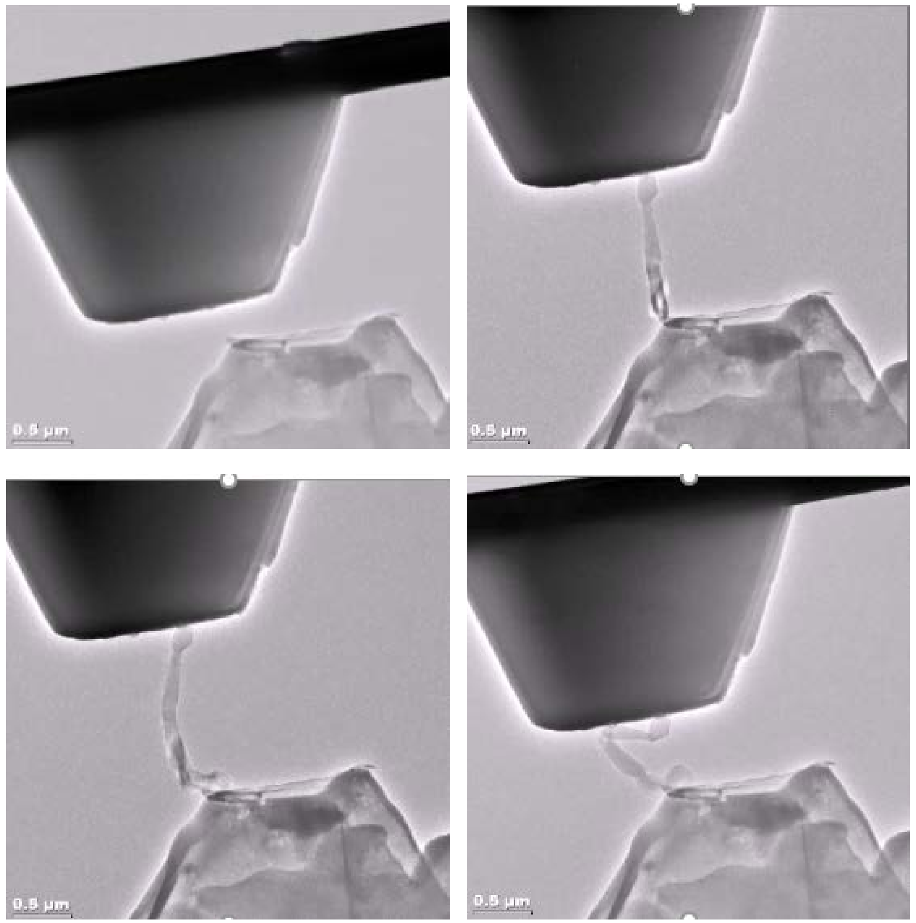
Critical stress versus whisker length (along the force direction) curves for mechanical yielding (pink), buckling (blue), kinking or the stopping of axial growth (cyan)

- During lithium whisker grows, it will encounter with the separator
- The suppression of separator will lead to the modification or failure of the growing lithium whisker
- The failure mode include bucking, kind formation, and lateral growth

Technical Accomplishments

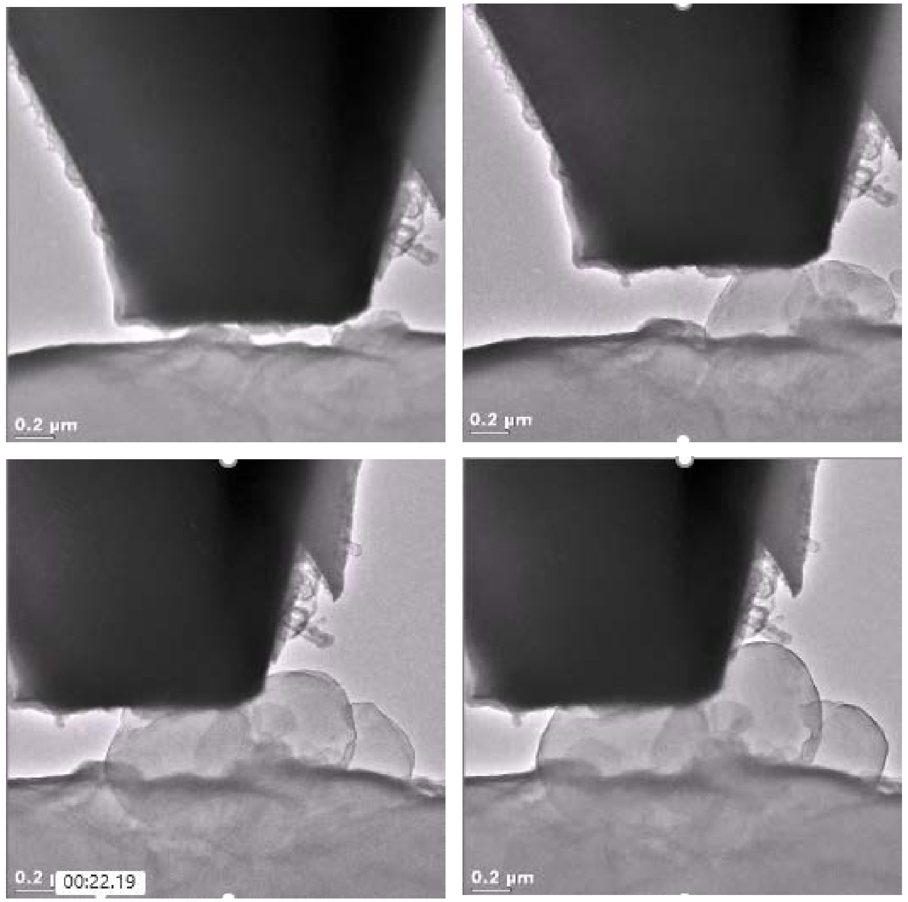
Comparison of Li dendrite nucleation and growth in CO_2 and N_2

Grown in CO_2 whisker morphology



- Sequential in situ TEM observation of the Li whisker “failure” by buckling

Grown in N_2 no whisker morphology

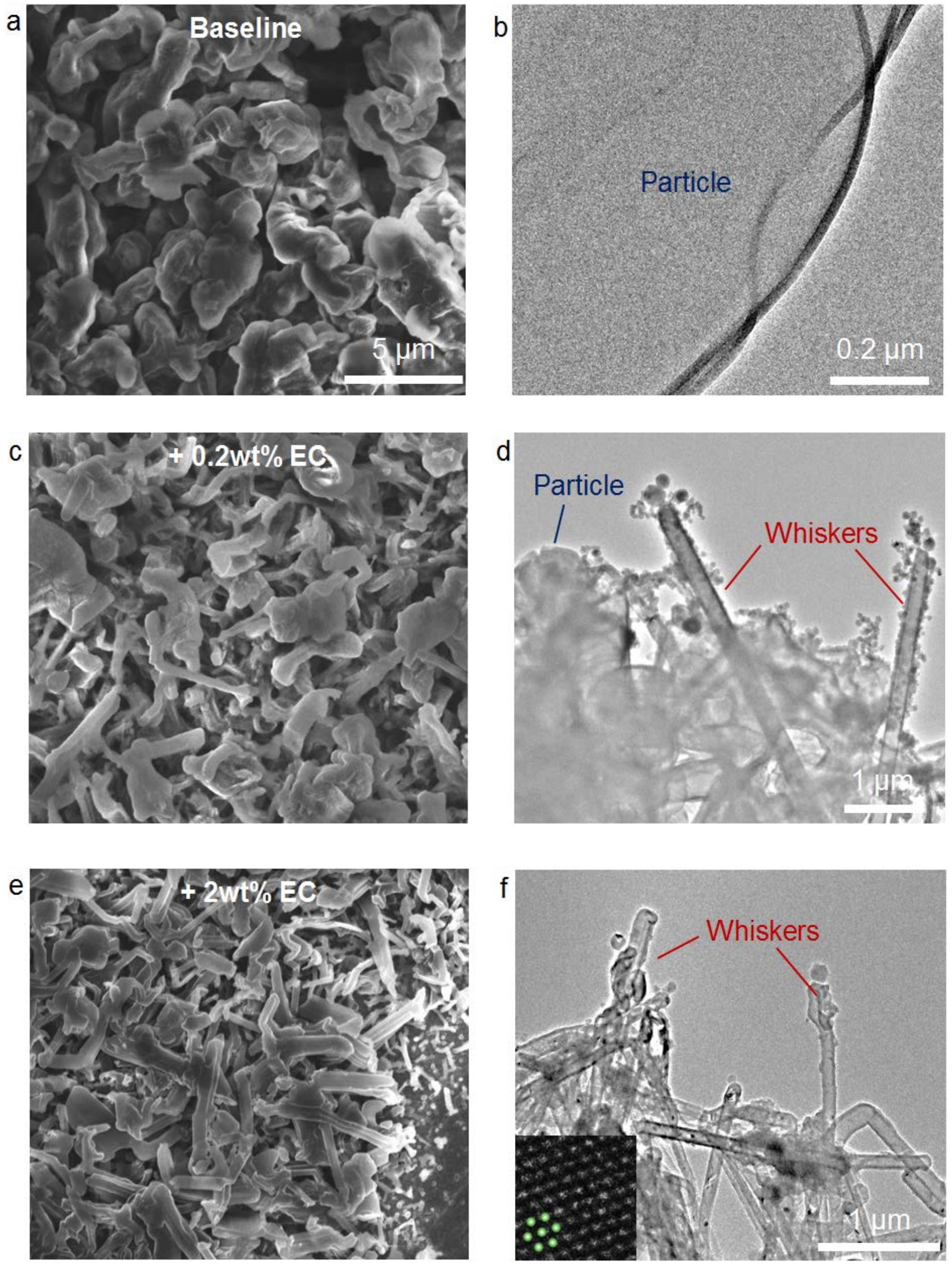


- Sequential in situ TEM observation of the Li deposition in N_2 environment

- The whisker morphology only develops in CO_2, but not in N_2
- SEI layer plays a key role
- Li_2CO_3 plays a key role

Technical Accomplishments

Testing of the in-situ TEM results using a coin cell



- Baseline electrolyte: 1 M LiFSI salt in Dimethoxyethane
- Li Particle

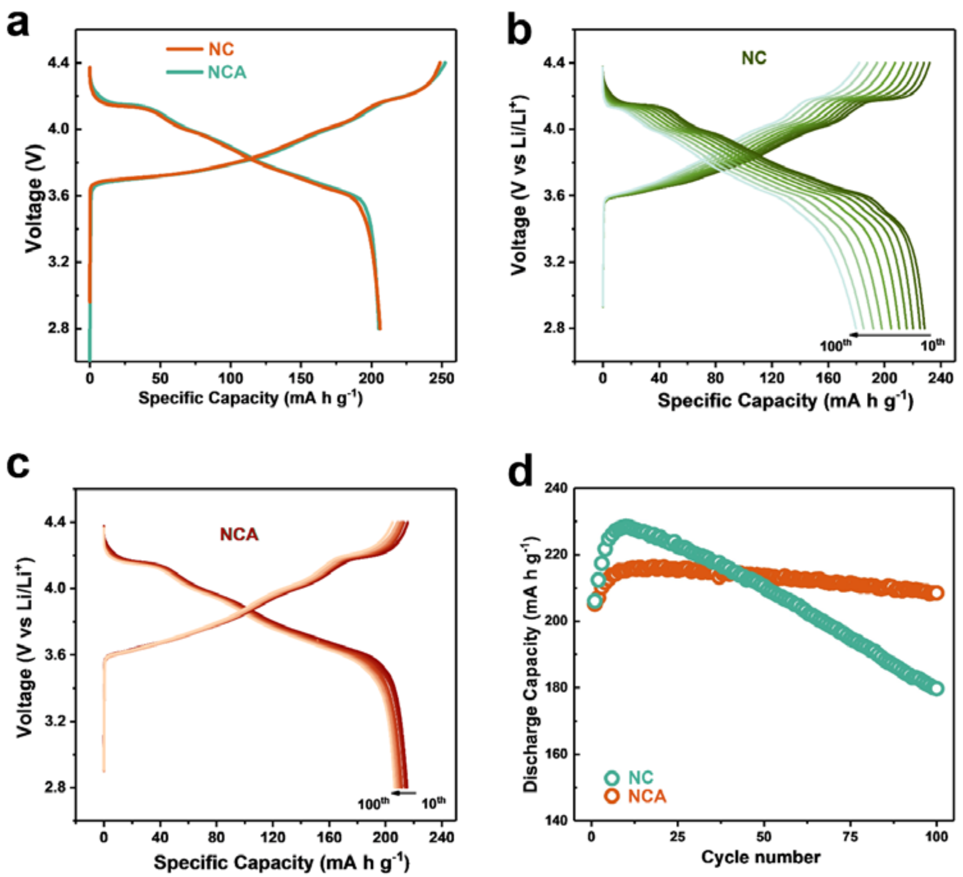
- Poisoning of the baseline electrolyte by adding 0.2% EC
- Coexistence both monolith and whisker

- 2% EC in the baseline electrolyte induces almost a dominance of Li whisker formation

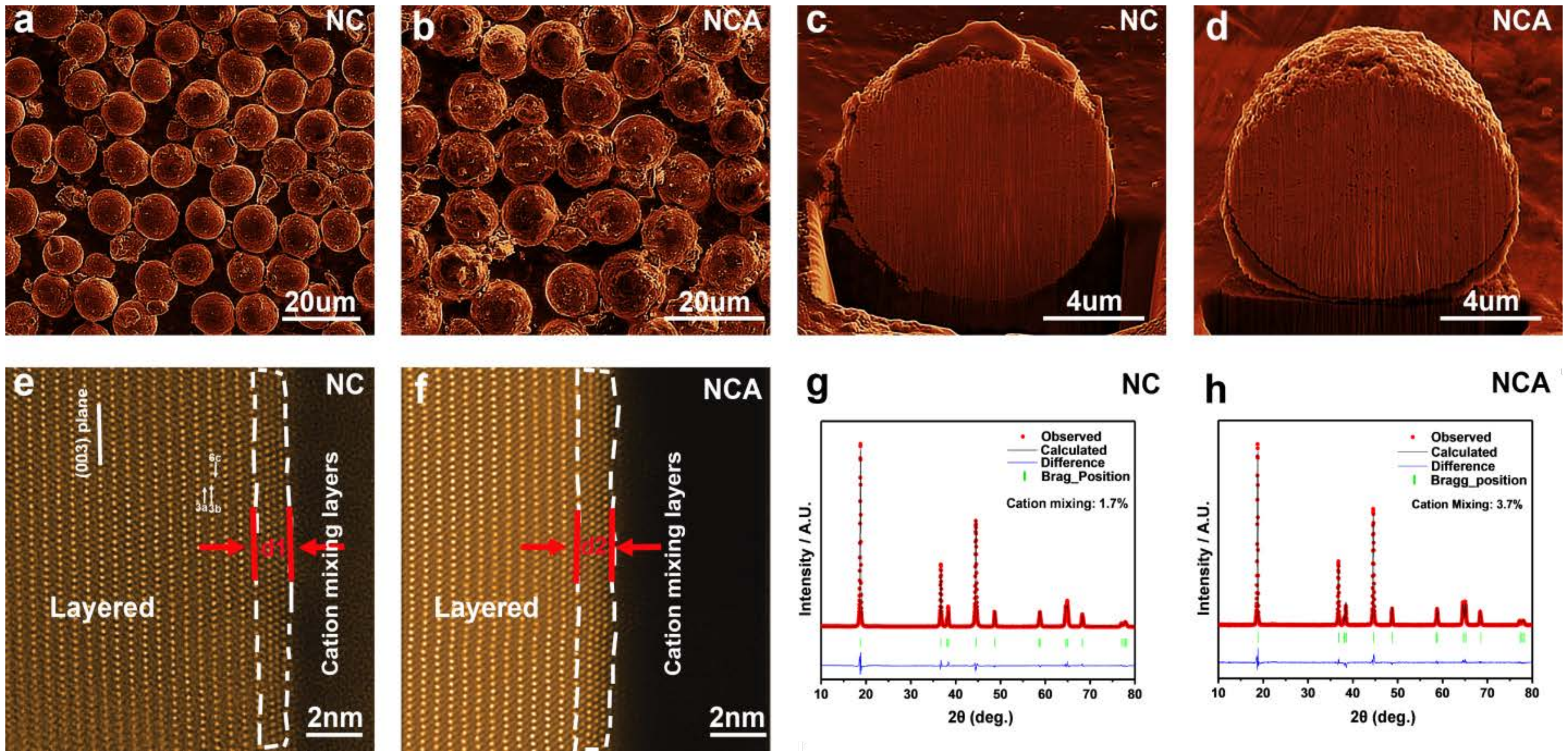
Technical Accomplishments

How does the dilute dopant of Al function to make it more stable?

$LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$ (NCA) shows stable cycling than $LiNi_{0.94}Co_{0.06}O_2$ (NC)



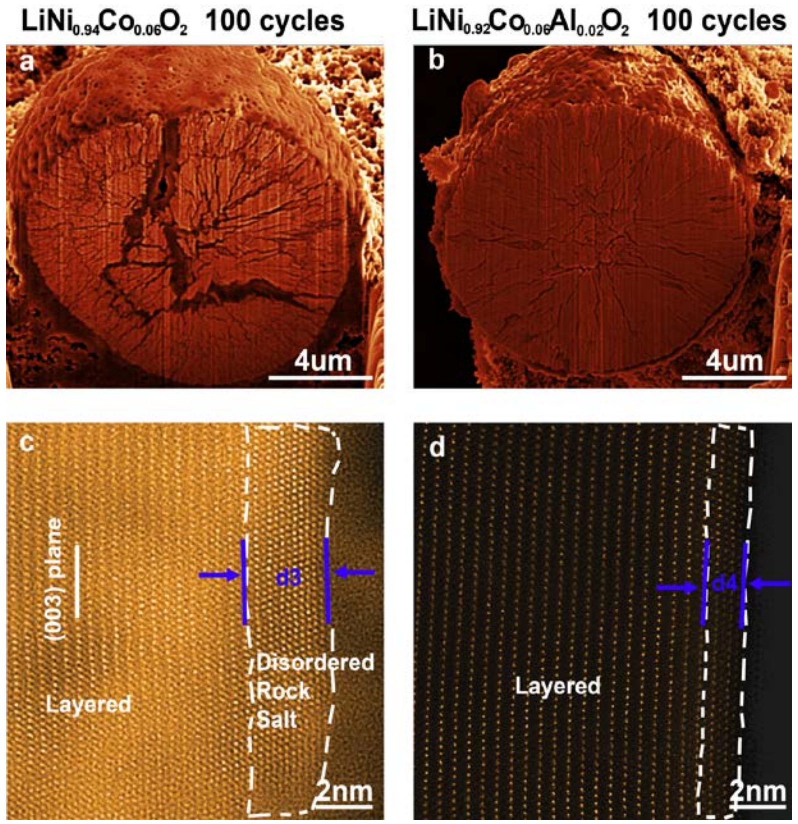
- Electrochemical cycling performance of $LiNi_{0.94}Co_{0.06}O_2$ (NC) and $LiNi_{0.92}Co_{0.06}Al_{0.02}O_2$ (NCA) measured in half-cell.

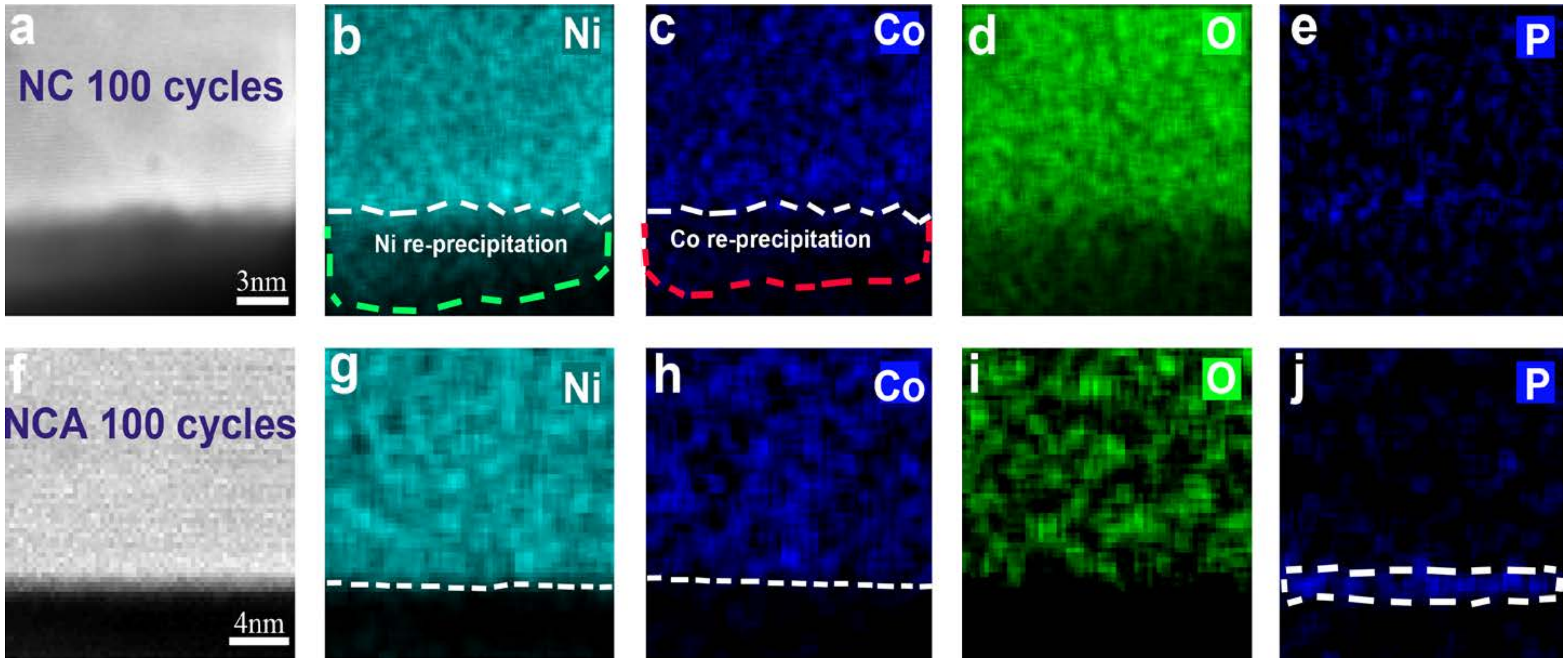


- Surface and bulk characterizations of NC and NCA pristine materials, showing no substantial difference

Technical Accomplishments

Structural and chemical features of NC and NCA and CEI layer



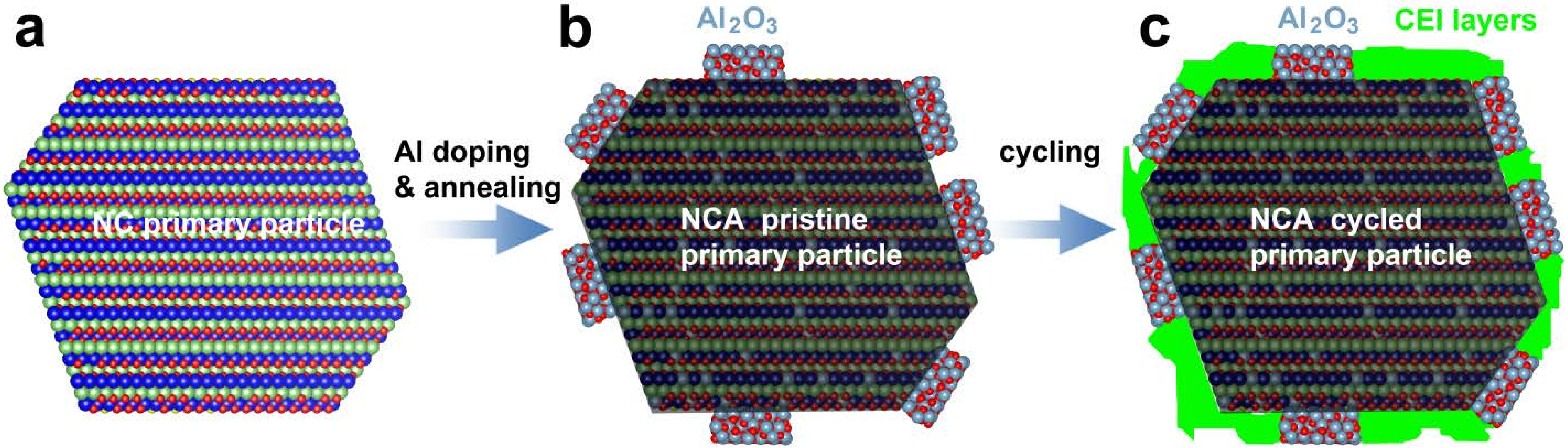


- Severe cracking of NC secondary particle after cycling
- A thicker dis-ordered rock salt structure on NC

- No stable CEI layer on NC
- TM re-precipitation on NC surface
- Formation of stable P containing CEI layers in NCA samples.

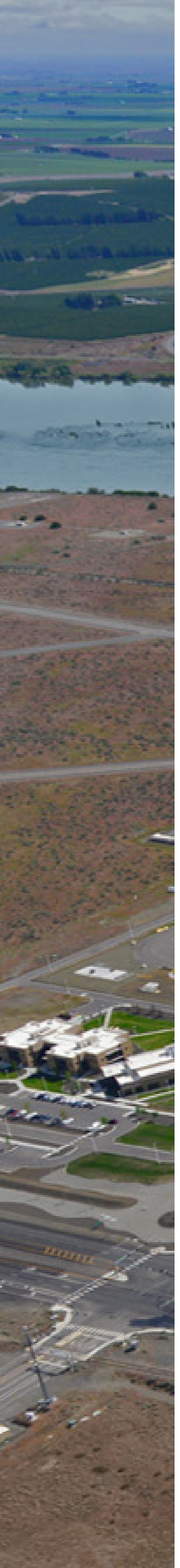
Technical Accomplishments

Schematic of the spatial distribution and function of Al in NCA



What we have concluded:

- Non-stable CEI layer on NC
- Dissolution of TM in NC
- Al in NCA is distributed in two ways: as surface Al_2O_3 and bulk solid solution
- Al_2O_3 is acting as a coating layer
- Al dissolved in the lattice leads to stable CEI layer



Responses to Previous Year Reviewers' Comments

- Made a poster presentation, the project was not reviewed in 2019

Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Laboratory: Preparation of cathode materials
- Lawrence Berkeley National Laboratory: Preparation of cathode materials
- Army Research Laboratory: Preparation of electrolyte
- Oak Ridge National Laboratory: Preparation of cathode materials
- Stanford University: Si nanowire-based anode and surface coating
- GM Research Center: Prepared porous Si, S enclosed in carbon
- National Renewable Energy Laboratory: ALD coated Si samples
- University of Texas at Austin: Preparation of cathode and anode materials
- Hummingbird Scientific: Help to develop the new TEM probe
- Thermo Fisher Scientific Company: ETEM capability development
- Group 14 Company: Si-C composite
- PNNL: Battery materials and battery cells
- Hydro Quebec: Si nanoparticle prepared by plasma techniques

Remaining Challenges and Barriers

- Due to the complicated steps of assembling the in-situ TEM cell, the reliability and reproducibility of the in-situ and operando TEM cell need to be improved.
- SEI layer beam sensitivity is still a big challenge. One way to address this problem is using cryo-TEM. At the same time, managing the electron dose rate is critical.
- Minimizing the liquid layer thickness to gain a better resolution in liquid cell. This can be achieved by designing of the liquid window geometry to minimize the bulging effect.
- For solid state battery, making a thin section that enables in-situ charge and discharging is critical to study interfacial process in solid state battery, while due to the thin section, the surface phenomenon needs to be addressed.

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Proposed Future Research

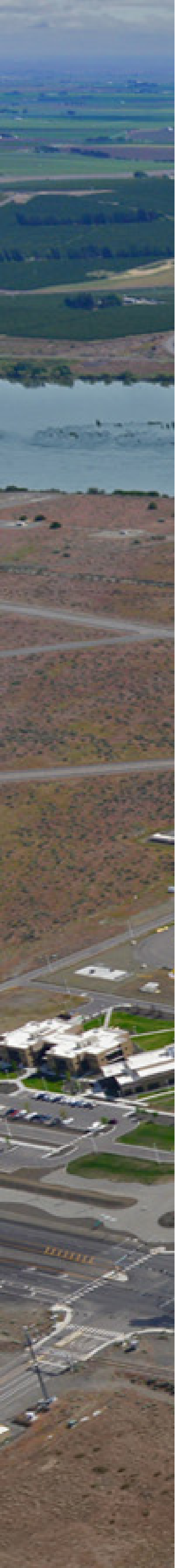
FY2020

- Reveal the effect of current density on the SEI layer structure and Li deposition morphology
- Reveal the effect of deposition voltage on the SEI layer structure and chemistry and morphological features of Li metal deposition

FY2021

- To reveal how does a Li metal fresh surface interact with electrolyte
- Using in-situ and cryo-TEM to determine why in the same electrolyte, some Li is whisker, while some as monolithic particle, gaining insights on the correlation of SEI and Li morphology
- Cryo-TEM and in-situ liquid SIMS determination of ionic transport characteristics in SEI layer
- In-situ and cryo-TEM reveal the correlation SEI layer structure with electrolyte structure and chemistry
- Reveal the structural and chemical evolution of interface in solid electrolyte/cathode and solid electrolyte/anode

Any proposed future work is subject to change based on funding levels



Summary

- Capture the nucleation and growth behavior of Li whiskers under elastic constraint, mimicking the interaction of Li whisker with a separator
- Li deposition is initiated by a sluggish nucleation of a single crystalline Li particle with no preferential growth directions
- SEI layer plays a decisive role in the Li morphology
- Retarded surface transport of Li plays a decisive role in the subsequent deposition morphology
- Lithium carbonate favors Li whisker formation
- The insights gained based on in-situ TEM is furfure validated in practical cells using a series of carbonate-poisoned ether-based electrolytes
- Mechanically, Li whiskers can yield, buckle, kink or stop growing under certain elastic constraints
- Revealed the functioning role of Al in NCA
- Answered the key question why NCA is more stable than NC even with very dilute Al in the system

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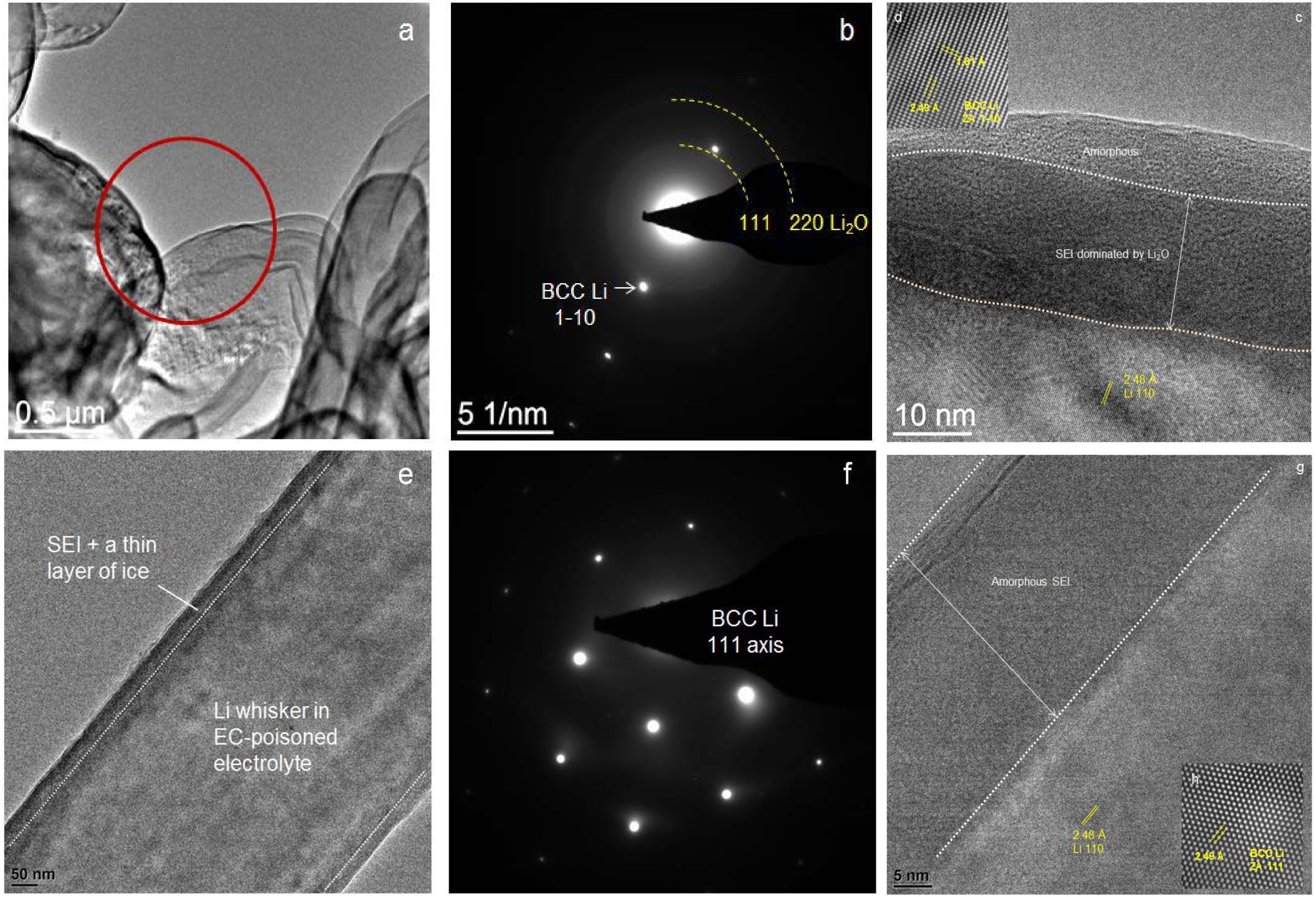
Technical Back-Up Slides

Cryo-TEM and electron diffraction characterization of the deposited Li and the SEI formed in 2wt% cyclohexanone-poisoned (a-d) and 2wt% EC poisoned (e-h) baseline electrolyte (1 M LiFSI salt in Dimethoxyethane).



a, e, Monolith and whisker morphology of the deposited Li, respectively. **b, f,** Selected area electron diffraction patterns of the deposited Li, showing clear evidence of Li_2O formation in cyclohexanone-poisoned electrolyte. **c, g,** High resolution cryo-TEM image showing the dominant Li_2O crystals in the SEI and amorphous phase dominated SEI, respectively. **d, h,** Filtered high resolution TEM image of the Li metal demonstrating the perfect BCC Li lattices.

Schematic Interpretation of the In Situ ETEM Observations